

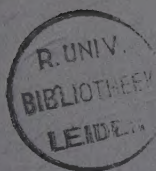
ELECTRONIC CONFIGURATION IN
ELECTRODEPOSITION FROM
AQUEOUS SOLUTIONS

BY

ERNEST HERBERT LYONS, JR.

B.S., Massachusetts Institute of Technology, 1931

M.S., California Institute of Technology, 1933



AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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Consideration of the electronic structures of metal ions shows that except for the platinum group, metals are not electro-deposited in aqueous solutions from ions having hybridized co-ordinate linkages involving the penultimate electronic shell. The energy required to break such "inner orbital" hybridization appears to be greater than that required for cathodic discharge of hydrogen from these solutions. The exceptional behavior of the platinum metals is probably the consequence of the extraordinary stability of the metallic state for these elements.

Inner orbital hybridization is also associated with absence of substitutional lability of the coordinated groups, although there are exceptions when the formation of addition intermediates is possible. The lability in outer orbital complexes is attributed to ready formation of a dissociation intermediate. Such an intermediate is probably also important in the cathode processes.

Where change in oxidation state between two ions does not involve alteration in configuration type, the reaction is electrolytically reversible. Where the configuration must be changed, the reaction is irreversible.

The deposition of each metal is considered in detail, and all reported observations considered reliable appear to support these conclusions. It is assumed that certain copper ions are of the outer orbital type although their planar configuration is ordinarily associated with inner orbital hybridization. Magnetic measurements are cited to support this assumption.

To test these conclusions experimentally, certain complexes of cobalt, copper, nickel, and zinc were examined at ordinary solid cathodes, and polarographically at dropping mercury and rotating platinum cathodes.

With *o*-phenanthroline, only the zinc complex has outer orbital configuration. The other complexes did not give electrodeposits; zinc deposits were obtained. With glycine, all of the complexes are outer orbital, and all give deposits. With sulfonated 8-quinolinol, the copper complex is the only inner orbital ion, and it is also the

only ion from which a metal deposit was not obtained. The naphthalène-1,8-diamino complex of nickel has inner orbital configuration, and the corresponding 1,2 complex outer orbital. Nickel is deposited only from the latter. Copper forms both types of complexes with dimethylglyoxime, depending on the pH, but the metal is deposited only from the outer orbital ion. Thus the original hypothesis was supported, and the existence of two types of copper complexes, only one of which will permit metal deposition, was demonstrated.

On the basis of these ideas, the Piontelli electrolytic classification of metals is explained and considerably expanded. The observation that for any metal, the aquo complex is the least reversible at the cathode is explained by the effect of the high activity of water on the dissociation of the ion.

By comparison with Pauling's formulations of the electron structures of the metallic state, it is shown that postulated dissociation intermediates have essentially the same configuration for "normal" metals. Consequently the reduction should require little activation, and should be reversible. This agrees with observation. The dissociation step amounts to the opening up of Pauling's "metallic orbital," and transfer of the discharging electrons can then occur essentially by ordinary metallic conduction processes. Before the reduction, the ion is probably linked to the cathode surface by one of the coordinating groups serving as a bridge. The bridge is then replaced by a metallic resonating bond. The dissociation intermediate serves to establish the bridge.

The ions of transition metals show half-vacant *d*-orbitals which must be filled when the ion is reduced to metal. This change in configuration is in accord with the observed irreversibility of the reductions. The activation involved represents excitation of electrons from hybridization resonance so that they may fill vacancies in the *d*-levels.

Inclusions in the deposits are residual coordinated groups. This explains the results of recent studies of their composition.

The parallelism between these considerations and the results of studies of electron-transfer reactions is striking, extending even to the probable activation steps. This is further support for the concepts proposed.

VITA

A native of Evanston, Illinois, Ernest Herbert Lyons, Jr., attended public schools there and in Kenilworth, Illinois. After three years at The Principia, he transferred to Massachusetts Institute of Technology where he received the Bachelor of Science degree in 1931. He was awarded the Master of Science degree by California Institute of Technology in 1933. Subsequently, as chief chemist of The Meaker Company, Chicago, he assisted in developing electrogalvanizing processes now in large scale use. During the war he worked on the development of the atomic bomb with the Manhattan District.

In 1947, he was appointed to the faculty of The Principia College, and during the same year, entered the Graduate College of the University of Illinois, where he studied summers. In 1951, he received an Atomic Energy Commission fellowship, and spent the following year in residence at Urbana. He is now at The Principia College.

His publications include: "The Comparative Ionizations of Selenic and Sulfuric Acids" (with M. S. Sherrill), *J. Am. Chem. Soc.* 54, 979 (1932); "The Photo-oxidation of Liquid Carbon Tetrachloride" (with R. G. Dickinson), *ibid.* 57, 443 (1935); "Anodic Cleaning," U. S. Pat. No. 2,092,130; "The Electrogalvanizing of Wire," *Trans. Electrochem. Soc.* 78, 317 (1940); "The Contamination and Electrolytic Cleaning of Cold Rolled Steel," *ibid.* 80, 361, (1941); "Acid Zinc Plating," *ibid.* 387; "What is a Clean Surface?" *ibid.* 88, 281 (1945).

